

## Phonon transport in imperfect $G_3H_2SO_4$ crystal

M Gaafar

Department of Physics, Faculty of Science, Alexandria University, Egypt

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**Abstract** : Effect of defects (X-ray irradiation, *L*-alanine admixture and iron sulphate doping) on the phonon thermal conductivity  $\lambda_{ph}$  of triglycine sulphate  $G_3H_2SO_4$  along the principal axes were studied, in the temperature range between 300 K and 350 K. The measurements exhibit that the effect of irradiation leads to slow increase, followed by rapid decrease of  $\lambda_{ph}$  around a threshold dose of irradiation ( $D_0 = 4 \cdot 10^3$  rad) in addition to Curie temperature  $T_c$ -shift towards lower temperatures. On the other hand, it is found that *L*-alanine admixture shifts  $T_c$  towards higher temperatures but  $Fe^{3+}$ -doping shifts it towards lower temperatures, associated with decrease of  $\lambda_{ph}$  in both the cases.

All of these defects produce broadening in the phase transition region which may be attributed to the compositional fluctuations and structural disorder in the solid solutions.

**Keywords** : Phonon transport, phase transition, imperfect triglycine sulphate

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Despite the complex chemical and crystallographic form of triglycine sulphate  $G_3H_2SO_4$ , it has become the object of active experimental research because of its basically simple ferroelectric character [1]. The previous work [2] dealt with phonon transport in pure  $G_3H_2SO_4$  crystals, hence measurements on the imperfect crystals is of current interest. Defects generated due to irradiation and doping in any crystalline lattice, generally cause deformation of the surrounding volume and modification of the local fields. The extent of the crystal deformation depends on the nature of the defect, its site in the crystal and the host-defect interaction. Detailed studies of the X-ray irradiated triglycine sulphate [3] showed that even very small doses can give large changes of its ferroelectric properties. It seems that there are slow relaxation processes associated with the defect motion which affect irradiated crystals [3].

On the other hand, the *L*-alanine molecule is sufficiently similar structurally and chemically to glycine molecule [4]. The effect of this organic admixture, as a symmetric organic molecule of glycine on  $G_3H_2SO_4$  compound, is lowering the permittivity and

shifting the Curie temperature  $T_c = 322\text{ K}$  of this compound towards higher temperatures [5,6]. Influence of dilute concentration of iron ions has been studied to show decrease of the thermal diffusivity of this compound [7].

The aim of this article is to outline the principal effects of inhomogenities of X-ray irradiation, *L*-alanine admixture and  $\text{Fe}^{3+}$ -ion doping on the phonon transport in triglycine sulphate.

Steady state method was used to measure the total thermal conductivity of  $\text{G}_3\text{H}_2\text{SO}_4$  and then the phonon part of the thermal conductivity  $\lambda_{ph}$  was deduced [2]. The pure samples [2] were irradiated at room temperature using X-ray source at 3 cm distance from the sample. Voltage of 30 KV and current of 15 mA were used for tube's operation. *L*-alanine admixed crystals were grown from aqueous solution of the compound with 0.2, 0.4, 0.6 weight % of *L*-alanine ( $\text{C}_2\text{H}_4\text{NH}_2\text{COOH}$ ).  $\text{Fe}^{3+}$ -doped crystals were grown from aqueous solution of the compound with the same weight % of iron sulphate  $\text{Fe}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$ . The concentration of *L*-alanine in the admixed crystals are  $n \cdot 10^{-4}$  ( $n = 3, 6, 8$ ) weight % and of iron sulphate in the doped crystals are  $m \cdot 10^{-4}$  ( $m = 3, 5, 7$ ) weight %.

Figure 1 shows the effect of X-ray irradiation with enhanced doses on  $\lambda_{ph}$  of the compound in *b*-direction at room temperature. It is clear that as the dose increases,  $\lambda_{ph}$  increases till the dose reaches its threshold value ( $D_0$ ), then it decreases rapidly (part AB and BC of the curve respectively). The slow increase of  $\lambda_{ph}$  for small doses ( $D < D_0$ ) is due to annealing effect of irradiation, which introduces structure relaxation and generates strain

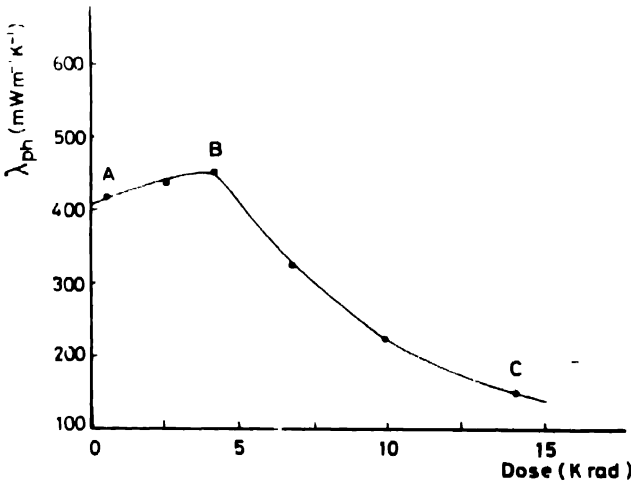


Figure 1. Variation of  $\lambda_{ph}$  of  $\text{G}_3\text{H}_2\text{SO}_4$  with X-ray doses at room temperature

induced regions [3]. For doses larger than the threshold value ( $D > D_0$ ),  $\lambda_{ph}$  starts to change markedly and decreases rapidly due to predominance of defect formation and release of such induced stress [8] which are effective for scattering. For demonstration of such induced stress, it has been suggested that the radiation damage effects might be

ascribed to a migration of the imperfections produced by the X-ray irradiation into the domain walls. This process is quite feasible as there is probably a strong mechanical stress field within or near a domain wall [8], which will provide favourable sites for some crystal imperfections.

Figure 2 shows that the X-ray irradiation introduced marked shift of the Curie temperature  $T_c$  towards lower temperatures and also increase of the transition region width ( $\Delta T$ ) with enhanced doses associated with decrease of peak's height.

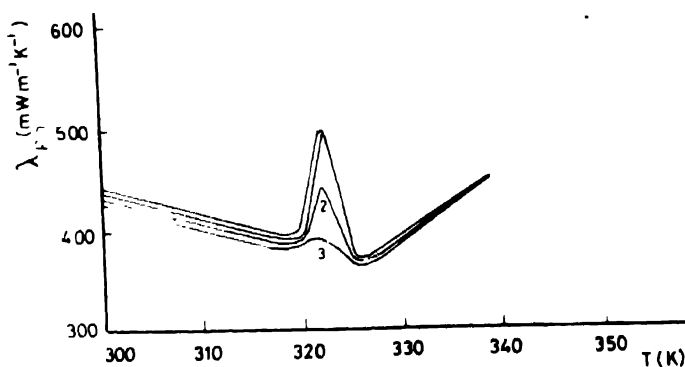


Figure 2. Temperature dependence of  $\lambda_{ph}$  of  $G_3H_2SO_4$  for various X-ray doses  $5 \cdot 10^3$ ,  $10 \cdot 10^3$ ,  $15 \cdot 10^3$  rad corresponding to curves 1, 2, 3 respectively

Figure 3 exhibits the effect of *L*-alanine admixture on  $\lambda_{ph}$  behaviour. The peak's height decreases and shifts to higher temperatures. Broadening of the phase transition region is also observed presumably and the spontaneous polarization due to the aligned defects at all temperatures above  $T_c$ , implies that a true paraelectric state does not exist in *L*-alanine admixed  $G_3H_2SO_4$  crystal [5].

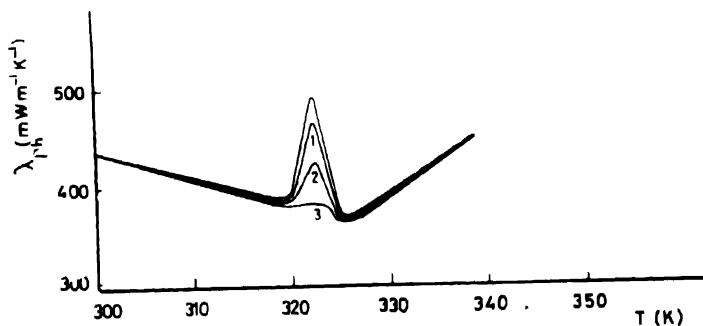


Figure 3. Temperature dependence  $\lambda_{ph}$  of  $G_3H_2SO_4$  for various *L*-alanine concentrations  $3 \cdot 10^{-4}$ ,  $6 \cdot 10^{-4}$ ,  $8 \cdot 10^{-4}$  weight % corresponding to curves 1, 2, 3 respectively.

Figure 4 shows the effect of  $\text{Fe}^{3+}$ -ions on decreasing  $\lambda_{ph}$ . This decrease depends on the admixture of the doped  $\text{Fe}^{3+}$ -ions in the crystal and thus their effect on the domain structure [7]. On the other hand, increase of  $\text{Fe}^{3+}$ -ions concentration decreases  $\lambda_{ph}$  (with about 10%  $\rightarrow$  20%  $\text{Fe}^{3+}$ ) shifts  $T_c$  towards lower temperatures and increases the phase transition region.

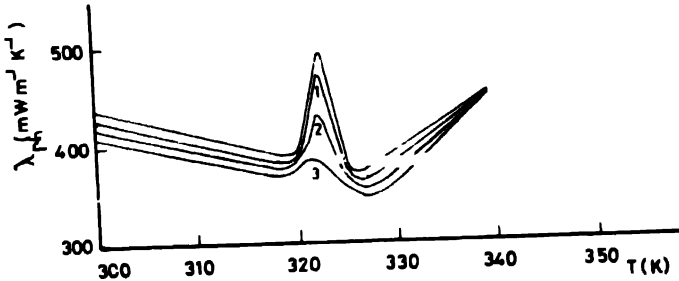


Figure 4. Temperature dependence  $\lambda_{ph}$  of  $\text{G}_3\text{H}_2\text{SO}_4$  for various iron sulphate concentration  $3 \cdot 10^{-4}$ ,  $5 \cdot 10^{-4}$ ,  $7 \cdot 10^{-4}$  per cent weight corresponding to curves 1, 2, 3 respectively.

In all cases of irradiation, admixture and doping, broadening of phase transition region is observed, and can be attributed to the compositional fluctuations and structural disorder in the solid solutions. However, when translational invariance (for perfect structural order) is destroyed as a result of structural disorder [9], broadening of the phase transition region occurs depending on the microscopic detail of this situation. Disordered systems cannot be described by a set of normal modes with well defined wavevectors  $q$ . In systems with major structural disorder, it is likely that the coupling with hopping defects is so strong that the lattice mode softening is essentially prevented altogether. Generally speaking, the effect of ionization radiation is similar to the effects of admixture and doping and can be accounted for in a similar manner.

In conclusion, X-ray irradiation of  $\text{G}_3\text{H}_2\text{SO}_4$  frozen in different phonon scattering mechanisms around the threshold dose, shifts  $T_c$  towards lower temperatures as  $\text{Fe}^{3+}$  ion doping does. *L*-alanine admixture shifts  $T_c$  towards higher temperatures. Broadening of phase transition region in all these cases of different defects, is attributed to creation of structural disorder in the solid solutions.

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